

CLAIMS:

1. A process for preparing an aqueous dispersion of water insoluble heteropolymeric particles comprising polymerising in an aqueous reaction medium ethylenically unsaturated monomers, said ethylenically unsaturated monomers comprising ionisable ethylenically unsaturated monomers and non-ionisable hydrophilic ethylenically unsaturated monomers, to form said heteropolymeric particles dispersed in said aqueous reaction medium,
wherein the monomers in said reaction medium at any point in time comprise less than 5 weight % of ionisable ethylenically unsaturated monomer,
wherein for at least a part of the polymerisation the monomers in said reaction medium have a composition which is maintained with an ionisable ethylenically unsaturated monomer content of from 0.5 to less than 5 weight % throughout polymerisation of at least 30 weight % of the total amount of monomers polymerised to form the heteropolymeric particles,
and wherein the total amount of non-ionisable hydrophilic ethylenically unsaturated monomers and ionisable ethylenically unsaturated monomers polymerised constitutes at least 75 weight % of the total amount of monomers polymerised to form the heteropolymeric particles.
- 20 2. The process according to claim 1, wherein the ionisable ethylenically unsaturated monomers comprise an ionisable acid group.
3. The process according to claim 2, wherein the ionisable ethylenically unsaturated monomers are selected from methacrylic acid, acrylic acid, itaconic acid, p-styrene carboxylic acids, p-styrene sulfonic acids, vinyl sulfonic acid, vinyl phosphonic acid, ethacrylic acid, alpha-chloroacrylic acid, crotonic acid, fumaric acid, citraconic acid, mesaconic acid and maleic acid.
- 25 4. The process according to claim 1, wherein the ionisable ethylenically unsaturated monomers comprise an ionisable basic group.

5. The process according to claim 4, wherein the ionisable ethylenically unsaturated monomers are selected from 2-(dimethyl amino) ethyl and propyl acrylates and methacrylates, and the corresponding 3-(diethylamino) ethyl and propyl acrylates and methacrylates.
- 5 6. The process according to any one of claims 1 to 5, wherein the non-ionisable hydrophilic ethylenically unsaturated monomers are selected from methyl methacrylate, ethyl acrylate, vinyl acetate, methyl acrylate, propyl acrylate, isopropyl methacrylate, hydroxy ethyl methacrylate, hydroxy propyl methacrylate.
7. The process according to any one of claims 1 to 6, wherein said at least a part of the polymerisation is a final part of the polymerisation.
- 10 8. The process according to any one of claims 1 to 7, wherein at any point in time during polymerisation the reaction medium comprises no more than 4 wt % of the ionisable ethylenically unsaturated monomers.
9. The process according to claim 8, wherein at any point in time during polymerisation the reaction medium comprises no more than 3 wt % of the ionisable ethylenically unsaturated monomers.
- 15 10. The process according to any one of claims 1 to 7, wherein the composition of the reaction medium is maintained with an ionisable ethylenically unsaturated monomer content of from 1 to less than 5 wt % throughout polymerisation of said at least 30 wt % of the total amount of monomers polymerised to form the heteropolymeric particles.
- 20 11. The process according to claim 10, wherein the composition of the reaction medium is maintained with an ionisable ethylenically unsaturated monomer content of from 2 to less than 5 wt % throughout polymerisation of said at least 30 wt % of the total amount of monomers polymerised to form the heteropolymeric particles.
- 25 12. The process according to any one of claims 1 to 11, wherein for said at least part of the polymerisation the reaction medium has a composition which is maintained

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with said ionisable ethylenically unsaturated monomer content throughout polymerisation of at least 55 wt % of the total amount of monomers polymerised to form the heteropolymeric particles.

13. The process according to claim 12, wherein the reaction medium has a composition
5 which is maintained with said ionisable ethylenically unsaturated monomer content throughout polymerisation of at least 75 wt % of the total amount of monomers polymerised to form the heteropolymeric particles.
14. The process according to any one of claims 1 to 13, wherein the total amount of
10 non-ionisable hydrophilic ethylenically unsaturated monomers and ionisable ethylenically unsaturated monomers polymerised constitute at least 80 wt % of the total amount of monomers polymerised to form the heteropolymeric particles.
15. The process according to claim 14, wherein the total amount of non-ionisable hydrophilic ethylenically unsaturated monomers and ionisable ethylenically unsaturated monomers polymerised constitute at least 85 wt % of the total amount
15 of monomers polymerised to form the heteropolymeric particles.
16. The process according to any one of claims 1 to 15 wherein the ethylenically unsaturated monomers which are polymerised to form the heteropolymeric particles further comprise hydrophobic ethylenically unsaturated monomers.
17. The process according to claim 16, wherein the total amount of hydrophobic monomers polymerised constitute no more than 20 wt % of the total amount of
20 monomers polymerised to form the heteropolymeric particles.
18. The process according to claim 17, wherein the total amount of hydrophobic monomers polymerised constitute no more than 10 wt % of the total amount of monomers polymerised to form the heteropolymeric particles.
- 25 19. The process according to claim 18, wherein the total amount of hydrophobic monomers polymerised constitute no more than 5 wt % of the total amount of monomers polymerised to form the heteropolymeric particles.

20. The process according to any one of claims 16 to 19, wherein the hydrophobic ethylenically unsaturated monomers are selected from styrene, alpha-methyl styrene, butyl acrylate, butyl methacrylate, amyl methacrylate, hexyl methacrylate, lauryl methacrylate, stearyl methacrylate, ethyl hexyl methacrylate, crotyl methacrylate, cinnamyl methacrylate, oleyl methacrylate, ricinoleyl methacrylate, vinyl butyrate, vinyl tert-butyrate, vinyl stearate and vinyl laurate.
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21. The process according to any one of claims 1 to 19, wherein the ethylenically unsaturated monomers further comprise polyfunctional monomers that are capable of introducing crosslinks to the polymeric structure of the heteropolymeric particles.
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22. The process according to claim 21, wherein the polyfunctional monomers are selected from glycerol propoxy triacrylate, glycerol propoxy trimethacrylate, ethylene glycol dimethacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, 2-isocyanoethyl methacrylate, N-methyl acrylamide, and glycidyl methacrylate or acrylate.
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23. The method according to any one of claims 1 to 15, wherein the monomers to be polymerised are introduced in two or more sequential feeds.
24. The process according to claim 23, wherein the first feed comprises less than 20 wt % of the total amount of ionisable ethylenically unsaturated monomer polymerised.
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25. The process according to claim 23 or 24, wherein the first feed comprises monomers which constitute at least 10 wt % of the total amount of monomers that are polymerised to form the heteropolymeric particles.
26. The process according to claim 25, wherein the first feed comprises monomers which constitute at least 30 wt % of the total amount of monomers that are polymerised to form the heteropolymeric particles.
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27. The process according to claim 26, wherein the first feed comprises monomers which constitute from 30 to 50 wt % of the total amount of monomers that are polymerised to form the heteropolymeric particles.
28. The process according to any one of claims 23 to 27, wherein the non-ionisable hydrophilic monomer is included in the first and second feeds.
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29. The process according to any one of claims 23 to 28, wherein the ethylenically unsaturated monomers which are polymerised to form the heteropolymeric particles further include hydrophobic ethylenically unsaturated monomers, and said hydrophobic ethylenically unsaturated monomers are only included in the second feed.
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30. The process according to claim 29, wherein the total amount of hydrophobic monomers polymerised constitute no more than 20 wt % of the total amount of monomers polymerised to form the heteropolymeric particles.
31. The process according to claim 30, wherein the total amount of hydrophobic monomers polymerised constitute no more than 10 wt % of the total amount of monomers polymerised to form the heteropolymeric particles.
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32. The process according to claim 31, wherein the total amount of hydrophobic monomers polymerised constitute no more than 5 wt % of the total amount of monomers polymerised to form the heteropolymeric particles.
- 20 33. The process according to any one of claims 29 to 32, wherein the hydrophobic ethylenically unsaturated monomers are selected from styrene, alpha-methyl styrene, butyl acrylate, butyl methacrylate, amyl methacrylate, hexyl methacrylate, lauryl methacrylate, stearyl methacrylate, ethyl hexyl methacrylate, crotyl methacrylate, cinnamyl methacrylate, oleyl methacrylate, ricinoleyl methacrylate, vinyl butyrate, vinyl tert-butyrate, vinyl stearate and vinyl laurate.
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34. The process according to any one of claims 23 to 33, wherein the ethylenically unsaturated monomers further comprise polyfunctional monomers that are capable

of introducing crosslinks into the polymeric structure of the heteropolymeric particles, and said polyfunctional monomers are only included in the second feed.

35. The process according to claim 34, wherein the polyfunctional monomers are selected from glycerol propoxy triacrylate, glycerol propoxy trimethacrylate, ethylene glycol dimethacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, 2-isocyanoethyl methacrylate, N-methyl acrylamide, and glycidyl methacrylate or acrylate.
36. The process according to any one of claims 23 to 35, wherein the polymer composition formed through polymerisation of monomer provided in the first feed has a number average molecular weight of less than about 60,000.
37. The process according to claim 36, wherein the number average molecular weight is less than about 50,000.
38. The process according to claim 37, wherein the number average molecular weight is less than about 40,000.
- 15 39. The process according to claim 38, wherein the number average molecular weight is less than about 30,000.
40. The process according to any one of claims 23 to 39, wherein the polymer composition formed through polymerisation of monomers provided in the first feed has a Tg of from about -50°C to about 100°C.
- 20 41. The process according to claim 40, wherein the Tg is from about 10°C to about 70°C.
42. The process according to claim 41, wherein the Tg is from about 10°C to about 50°C.
43. The process according to any of claims 23 to 42, wherein the polymer composition formed through polymerisation of monomers provided in the second feed has a Tg of from about -50°C to about 100°C.

44. The process according to claim 43, wherein the Tg is from about -10°C to about 70°C.
45. The process according to claim 44, wherein the Tg is from about 0°C to about 40°C.
- 5 46. The process according to any one of claims 1 to 45, wherein the average particle size of the heteropolymeric particles formed is less than about 200 nm as measured by capillary hydrodynamic fractionation.
47. The process according to any one of claims 1 to 46, wherein the aqueous dispersion is subsequently thickened by introducing an ionising agent to the dispersion.
- 10 48. A method of preparing a paint comprising combining conventional paint additives with the aqueous dispersion of water insoluble heteropolymeric particles prepared according to the process of any one of claims 1 to 46.
49. The method according to claim 48, wherein the paint is thickened through the introduction of an ionising agent to the paint.
- 15 50. An aqueous dispersion of water insoluble heteropolymeric particles, said heteropolymeric particles comprising polymerised ionisable ethylenically unsaturated monomers and polymerised non-ionisable hydrophilic ethylenically unsaturated monomers,
wherein the polymerised ionisable ethylenically unsaturated monomers are present
20 in an amount of less than 5 weight % throughout the polymeric composition of the heteropolymeric particles,
wherein a segment which represents at least 30 weight % of the heteropolymeric particles has a polymeric composition which comprises no less than about 0.5 weight % and less than 5 weight % of polymerised ionisable ethylenically unsaturated monomers, based on the total weight of monomers polymerised to form
25 the segment,
and wherein the combined amount of polymerised ionsiable ethylenically

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unsaturated monomers and non-ionisable hydrophilic ethylenically unsaturated monomers constitute at least 75 weight % of the heteropolymeric particles.